A New Compilation of Gas and Steam Analyses from The Geysers Geothermal Field, California, USA

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SUMMARY- Herein, we summarize the results of our recent compilation of well discharges from The Geysers geothermal field. H_2 and H_2S concentrations are highest in the Southeast Geysers, where steam samples have δD and $\delta^{18}O$ values that reflect replenishment by meteoric water. In the Northwest Geysers, samples are enriched in gas/steam, CO_2, CH_4, and N_2/Ar relative to the rest of the field, and contain steam that is elevated in δD and $\delta^{18}O$, most likely due to substantial contributions from Franciscan-derived fluids. The $\delta^{13}C$ signature of CO_2, trends in CH_4 vs. N_2, and abundance of NH_3 indicate that the bulk of the non-condensable gases are derived from thermal breakdown of organic materials in Franciscan meta-sediments.

1. INTRODUCTION

Despite the prominence of The Geysers as the world's largest geothermal field (formerly producing at ~2000 MWe), there are very few published chemical analyses of steam and non-condensable gas (Allen and Day, 1927; Nehring, 1981; Truesdell et al., 1987). Recently, Lowenstern et al. (1999) published a USGS Open-File Report with the first detaileed geochemical analyses of well discharges from The Geysers steam field. Below, we summarize the data and discuss some of the key geochemical trends. Our discussion focuses primarily on the sources of steam and non-condensable gases in the geothermal fluids.

2. THE GEYSERS STEAM FIELD

The Geysers is a vapor-dominated geothermal field (Fig. 1) located within the Mayacamas Range in northern California, about 150 km north of San Francisco and at the margin of the Clear Lake volcanic field (Hearn et al., 1981). In vapor-dominated systems, water is present both as liquid and steam, though vaporized water constitutes the pressure supporting phase (White et al., 1971). The present system is believed to have boiled down from a previous liquid-dominated reservoir about 0.28 Ma (Moore and Gunderson, 1995; Hulen et al., 1997; Moore et al., 1998). The Geysers geothermal system was apparently initiated by heat from a composite granitoid intrusion ("the felsite"; Schriener and Suemnicht, 1981) emplaced about 1.1 Ma; and the system has since been sustained by subsequent (unsampled) intrusions (Kennedy and Truesdell, 1996; Grove et al., 1998). Though part of the geothermal reservoir is located within the felsite, most is hosted by Franciscan complex meta-sediments.

At the wellhead, The Geysers steam is superheated; however, within the deeper reservoir, H_2O is contained both as steam and interstitial liquid. Well discharges are thus a function of the relative amounts of the two phases available for transport to the surface (Truesdell et al., 1987). D'Amore and Truesdell (1985) found that y (the proportion of steam to that of liquid water + steam) was very low in the Southeast Geysers (y = 0.01 to 0.05), whereas fluids from the Northwest Geysers were predominantly derived from reservoir steam (y = 0.1 to 1.0). These fieldwide characteristics can partially be traced to different temperature reservoirs that have been identified. In the Northwest and north-Central Geysers, the steam field is divided into two principal reservoirs, a normal-temperature reservoir and a high-temperature reservoir (NTR and HTR), which appear to be hydrologically connected (Walters et al., 1992). In the NTR, temperatures are close to 240°C with a pressure around 35 bars. Pressures in the underlying HTR are similar, though temperatures normally exceed 300°C and have been measured as high as 342°C (Walters et al., 1992). Wells that extend into the HTR pass through the NTR, so that sampled fluids represent a mixture of steam and gas from both reservoirs. Kennedy and Truesdell (1996) conjecture that the low y and lack of evidence for the HTR in the Southeast Geysers may be due to the greater meteoric recharge and greater heat loss by conduction due to the shallower reservoir depths. Geochemically, there are a number of obvious trends that differentiate the Southeast Geysers from the Northwest Geysers. Steam discharges in

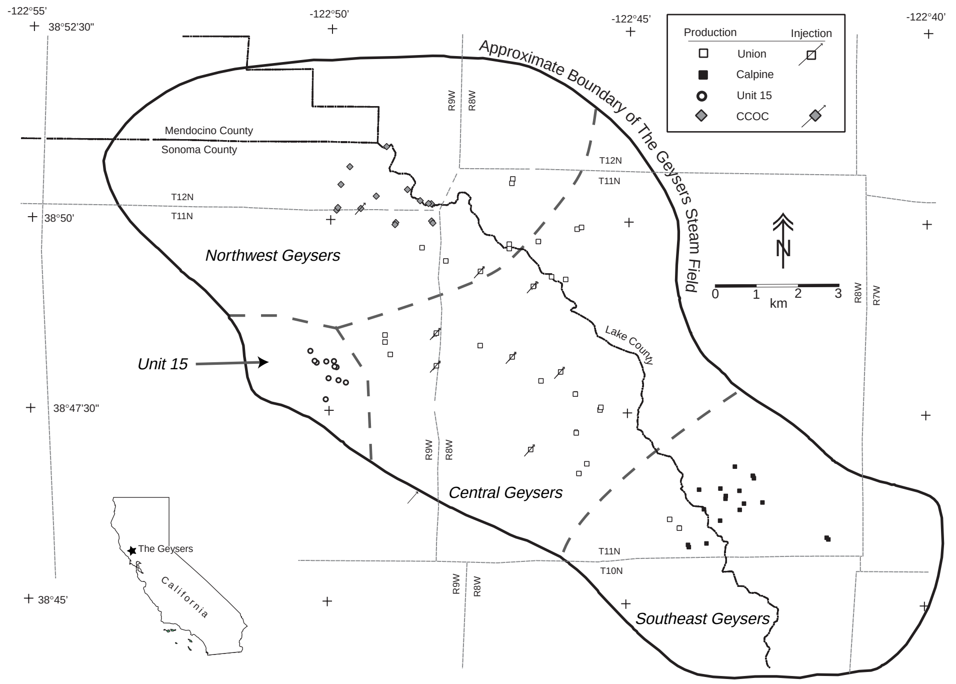

Figure 1. Well locations for this study. Symbols correspond to geothermal operator at time of sampling. Gray lines indicate informal region boundaries that separate the field into Southeast, Central, Northwest and Unit 15 sectors. They are not necessarily consistent with terminology used in other studies.

the Southeast Geysers have an isotopic signature that is similar to present-day springs and streams in the region (Truesdell et al., 1987). In contrast, samples from the Northwest Geysers have enriched $\delta^{18}O$ and δD values and show far less influence of present-day meteoric water. Haizlip (1985) suggested that this isotopically enriched water was equivalent to "connate" or formation waters that originate from Franciscan and Great Valley sediments and are found throughout the Clear Lake volcanic field (White et al., 1973).

The Northwest Geysers is also characterized by higher gas/steam ratios than the rest of the field (Truesdell et al., 1987; Walters et al., 1992). This may be due partially to: 1) the high temperatures associated with the HTR, causing greater breakdown of organic matter in Franciscan rocks, and 2) to the lesser flushing by meteoric water over the lifetime of the system (Gunderson, 1992). Steam from the Northwest Geysers and parts of the Central Geysers is also elevated in HCl (Haizlip and Truesdell, 1989), which has caused considerable corrosion-related problems. Lastly, gas samples from the Northwest Geysers have high $^{3}He/^{4}He$ ratios (R/Ra of 6.3 to 8.3; Kennedy and Truesdell, 1996), up to values typical of mid-ocean-ridge basalt (MORB). Kennedy and Truesdell (1996) interpreted these values to indicate present-day magma degassing beneath the Northwest Geysers, possibly extending south underneath the entire geothermal field.

3. METHODS

Sampling procedures are described in detail by Fahlquist and Janik (1992) and Lowenstern et al. (1999). All samples were taken directly from the sampling port on an insulated steam line near the wellhead at iso-enthalpic conditions with acid mitigation systems deactivated to prevent sample contamination and to ensure minimal condensation of fluid in the wellbore prior to sample collection. The fluid was drawn into an evacuated bottle containing 4N NaOH solution.

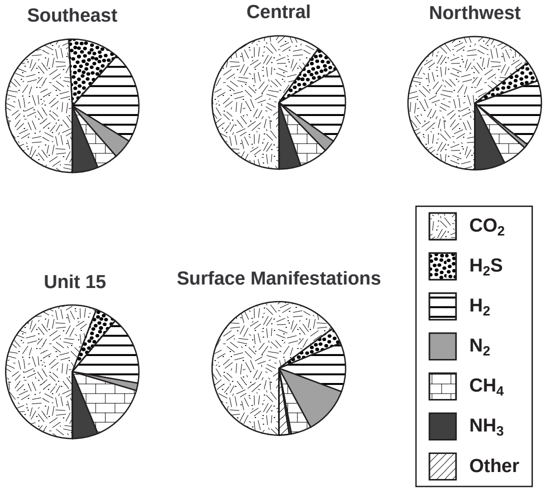

Figure 2. Relative amounts of various non-condensable gases in The Geysers well discharges.

Samples were analyzed by a combination of gas chromatography (N_2, Ar, He, O_2, CH_4 and H_2), gravimetry/volumetry (CO_2, H_2O and H_2S), selective-ion electrode (NH_3) and mass spectrometry ($\delta^{13}C$-CO_2). Steam was also collected as condensate for isotopic analysis of $\delta^{18}O$ and δD.

4. RESULTS

Lowenstern et al. (1999) provides information on sample locality, well and casing depths, gas geochemistry and isotopic composition for 81 well discharges. In addition, they provide data for nine re-injected steam condensates and five surface manifestations (fumaroles and bubbling/boiling pools). This published dataset is likely to vary somewhat from present-day compositions at The Geysers which are affected by re-injection of steam condensate and treated wastewater, and by long-term pressure declines (Beall et al., 1992; Beall and Box, 1993).

Gas to steam ratios (ppm by weight) averaged 630 in wells from the Southeast Geysers; in contrast, they averaged 3,250 in the Central Geysers, 21,650 in the Northwest Geysers and 10,260 in Unit 15 wells (Table 1). Looking only at the non-condensable gas compositions, Southeast Geysers wells had higher relative H_2S and H_2, and lower CO_2 than the other parts of the field (Fig. 2). The total of CO_2 + CH_4 + NH_3 was highest in the Northwest Geysers and Unit 15.

5. DISCUSSION

We observe two basic types of gases from The Geysers. The first is high in CH_4, CO_2, gas/steam and N_2/Ar, and is common in the Northwest Geysers. The other type is found in the Southeast Geysers. It is lower in CO_2 and CH_4, and higher in H_2S and H_2 (see Fig. 3). N_2/Ar values are closer

Table 1. Mean compositions of well discharges.

	SE	C	NW	U15	Surf.
Gas/Steam	630	3250	21,650	10,260	---
CO_2 (mol%)	49.0	59.7	65.0	56.0	64.9
H_2S (mol%)	12.3	6.72	4.91	5.35	3.88
He (mol%)	0.0161	0.0077	0.0014	0.0004	0.0021
H_2 (mol%)	22.3	18.6	15.9	16.7	11.9
O_2 (mol%)	0.0135	0.046	0.0081	0.0375	2.30
Ar (mol%)	0.058	0.0237	0.0075	0.017	0.204
N_2 (mol%)	4.66	2.96	1.04	1.76	11.5
CH_4 (mol%)	5.14	6.99	6.06	14.3	4.86
NH_3 (mol%)	6.19	5.33	7.24	6.21	0.512
N_2/Ar	118	157	239	169	58
δD H_2O (‰)	-53	-49	-47	-49	
$\delta^{18}O$ H_2O(‰)	-5.1	-4.3	-1.4		
$\delta^{13}C$ CO_2 (‰)	-13.5	-13.3	-12.4	-12.7	-13.1

SE= Southeast Geysers; C= Central; NW= Northwest; U15 = Unit 15; Surf. = Surface Manifestations. Gas/Steam in ppm by weight.

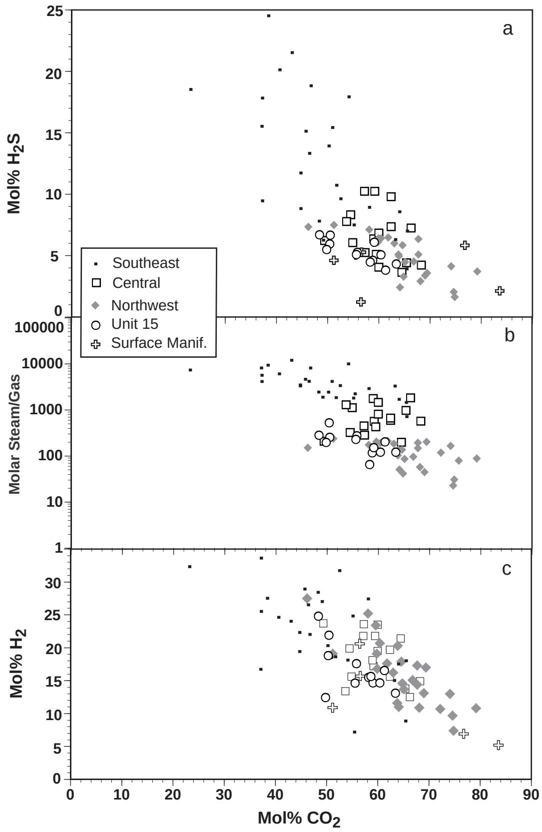

Figure 3. Mole % CO_2 versus (**a**) H_2S, (**b**) molar steam/gas and (**c**) H_2 for The Geysers wells and surface manifestations.

to those of air and air-saturated water (Table 1).

Several sources of gases and steam are evident at The Geysers. Most Southeast Geysers well discharges have $\delta^{18}O$ between –5 and –7 ‰ and δD between –50 and –60 ‰, consistent with slightly ^{18}O-shifted meteoric water (Fig. 4). Other Southeast Geysers samples trend toward the composition of evaporated steam condensate that has been re-injected. In contrast, samples from the Northwest Geysers with their high CO_2, CH_4 and gas/steam, relatively high NH_3, and low H_2S and

H_2, have characteristics that imply a strong component of fluid from the HTR (Walters et al., 1992). In samples with the highest gas/steam ratios, and thus the greatest signature from the HTR, the steam is enriched in an isotopically heavy component (Fig. 4). Such a trend has been noted before and attributed as due to either introduction of magmatic fluids (e.g., D'Amore and Bolognesi, 1993) or connate/Franciscan waters (Haizlip, 1985) similar to those found in the Clear Lake volcanic field and surrounding region (White et al., 1973; Goff et al., 1995).

We interpret the gas abundances and ratios of Northwest Geysers samples to be most consistent with their derivation in large part due to thermal breakdown of organic materials in Franciscan-hosted sediments and conclude that the trend in δD and $\delta^{18}O$ is also best explained by such an origin. Strongly supporting this "Franciscan" signature is the $\delta^{13}C$ of CO_2 in the Geysers samples, which is very similar throughout the field, ranging only from –11.7 to –15.0 ‰ VPDB (most are between –12 and –14‰). Bergfeld et al. (1999) found that such values are typical of Franciscan carbonate veins and concluded that gas at The Geysers has derived its carbon primarily from these older metamorphic calcite veins, mixed with some carbon from organic materials in the Franciscan rocks. A significant magmatic carbon input to the system could only be allowed if magmatic carbon in this setting were somewhat lighter in $\delta^{13}C$ than the typical MORB values of –4‰ to –8‰.

Another characteristic consistent with a crustal source of CO_2 in The Geysers reservoir is the high CH_4 and NH_3 concentrations throughout the field and particularly in the high gas/steam wells of the Northwest Geysers. These two gases are unstable at magmatic temperatures and crustal oxidation states and are typically added to geothermal and volcanic discharges by breakdown of sedimentary and metamorphic sources at relatively low-temperatures (Symonds et al., 1994). Such sources could supply the abundant CO_2 as well.

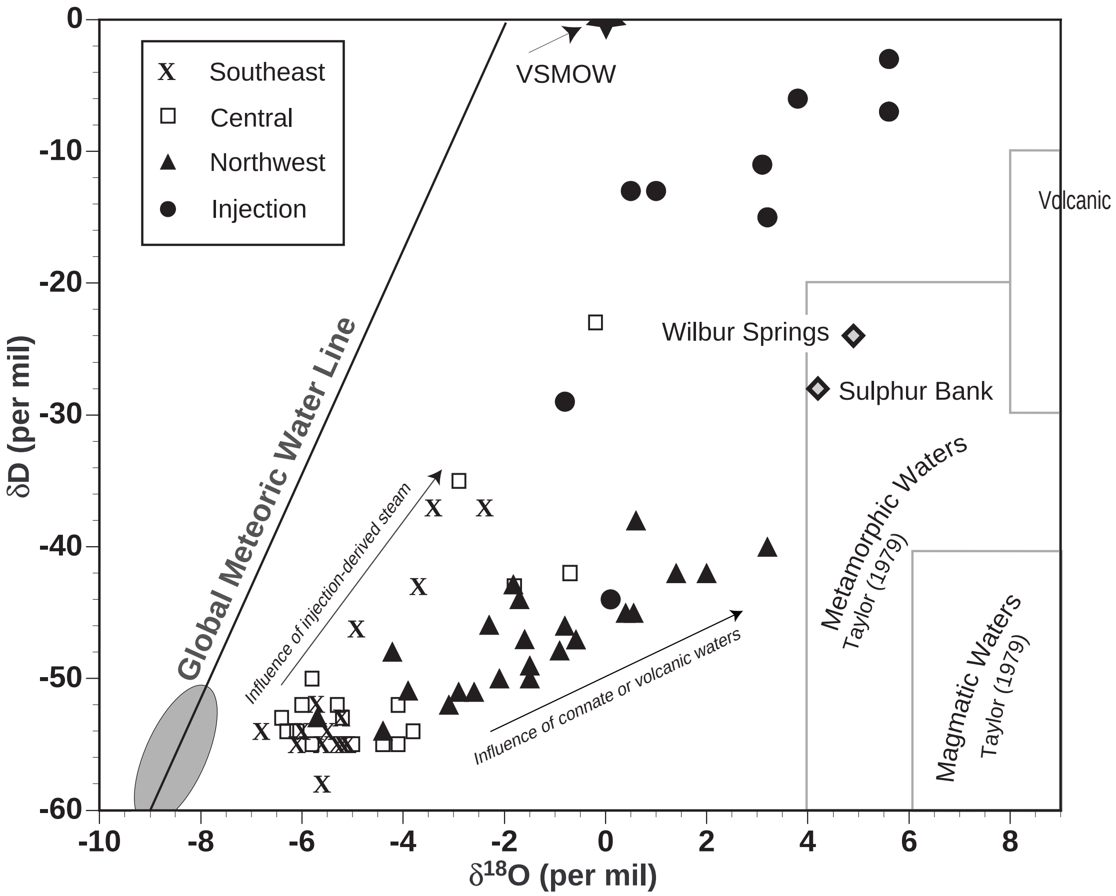

Figure 4. $\delta^{18}O$ versus δD for steam condensed from The Geysers wells. Samples from wells of the Southeast Geysers plot close to the global meteoric water line and local meteoric water (gray ellipse), as do some samples from the Central Geysers. Some of these wells plot on a trend toward injection-derived condensate. Samples from the Northwest Geysers form a trend toward an isotopically heavy end-member similar to connate or volcanic waters. References used to construct the diagram are listed in Lowenstern et al. (1999).

N_2/Ar ratios exceed 300 in 7 samples, 6 of which are from high gas/steam wells from the Unit 15. These values are far greater than the atmospheric ratio of 84 and are comparable to N_2/Ar found in many springs and gas vents from the Clear Lake volcanic field, as discussed by Goff et al. (1995). Jenden et al. (1988) report N_2/Ar for natural gases from deep wells in the California Great Valley that range from >200 to several thousand, with one sample having a ratio of 22,000. These extraordinarily high values were attributed to production of N_2 by thermal decomposition of organic matter and/or oxidation of ammonium in sheet silicates of the Franciscan assemblage believed to underlie the host strata. High N_2/Ar can also be associated with an arc-magmatic signature, where sedimentary materials are transferred to the mantle wedge either during subduction or magma ascent (Giggenbach 1992). However, at The Geysers, N_2 is correlated with non-magmatic CH_4 (Lowenstern et al., 1999), consistent with derivation of N_2 from breakdown of Franciscan meta-sediments.

We conclude that the CH_4, and NH_3 abundances, N_2/Ar, gas/steam ratios, and stable isotope geochemistry of samples from the Northwest Geysers are best explained as reflecting a Franciscan meta-sedimentary source (White et al., 1973; Haizlip, 1985). Convincing evidence for the continuing presence of mid-crustal magma chambers in this region is indicated by: 1) the young volcanism of the Clear Lake volcanic field, 2) the presence of a large, hot, and shallow geothermal system, and, 3) the high $^3He/^4He$ in gases from many Northwest Geysers wells (Kennedy and Truesdell, 1996). Nevertheless, it appears that the steam and gas at The Geysers, with the exception of He, is still derived primarily from meteoric and meta-sedimentary sources.

6. CONCLUSIONS

- ♦ The geochemistry of wells from The Geysers is strongly correlated with location. Samples from the Northwest Geysers are high in CO_2, CH_4, NH_3, N_2/Ar and gas/steam ratios. Those from the Southeast Geysers are enriched in H_2S and H_2 and contain steam isotopically similar to local meteoric water or re-injected steam condensate.
- ♦ Chemical and isotopic characteristics of discharges from the Southeast Geysers indicate greater meteoric recharge to that part of the field and a longer history of water-rock interaction (Gunderson, 1992; Truesdell et al., 1987).
- ♦ Gas chemistry and isotopic characteristics of samples from The Geysers are consistent with a strong meta-sedimentary source, likely caused by boiling of connate waters and thermal breakdown of sedimentary organic materials and vein minerals within or beneath the reservoir. Such processes are most obvious in the Northwest Geysers where there is a greater thickness of Franciscan sediments, less meteoric recharge, and evidence for recent magmatic heating.

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